Photoelectron spectroscopy of GdO^-

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We present vibrationally resolved photoelectron spectra of the gadolinium oxide anion GdO^- using 3.495-eV photons. The molecules have been produced in a laser vaporization source and have been mass selected prior to the detachment process. An electron affinity of 1.19 ± 0.1 eV is measured. The vibrational frequencies of the ground state and the first excited state are determined to be 790 ± 40 and 887 ± 40 cm^{-1}, respectively. A group of states at 2.6-eV binding energy is interpreted to correlate with the $4f^7(^8S)\ 6p(^2P_{1/2})\ |\Omega_{6p}| = 1/2$ configuration.

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I. INTRODUCTION

The application of the ligand field theory (LFT) to the diatomic lanthanide (L) oxides has been very successful in the past [1], since these molecules exhibit a strongly ionic character. In the simplest approximation, the ligand is supposed to have a closed-shell structure, and in the case of the lanthanide oxides this means an $L^{2+}O^{2-}$ molecule. The molecular electronic structures are derived from the states of free L^{2+} ions that are disturbed under the influence of the O^{2-} ligand electric field. However, this oversimplified model fails to motivate the existence of electronic states with higher multiplicity, as, for example, the low-lying quartet states in LaO [2]. The explanation of these states within the LFT framework requires an internal structure of the ligand, namely an open-shell configuration.

Gd and La are distinguished by their $4f$ occupation. La has no $4f$ electron in its ground state, whereas Gd has a half-filled $4f$ shell which to a large extent remains unaffected by chemical bonding due to the localized character of these states [3]. One might be tempted to assume that the low-lying energy levels of the respective oxides could be related to each other. In the case of LaO, the lowest excited states correspond to configurations in which the unpaired $6s$ ground-state electron climbs up the ladder of $5d$-derived states that have been split into σ, δ, and π states due to the bonding [2,4,5]. In contrast, the low-energy levels of GdO are derived from $6p \leftarrow 6s$ excitations [6].

GdO has been investigated previously using electron-spin resonance (ESR) [7] and infrared spectroscopy (IR) [8] in an Ar matrix and wavelength-resolved fluorescence excitation laser spectroscopy (gas phase) [6]. These experiments have established a $^9\Sigma$ ground state ($Gd^{2+}[4f^7(^8S)\ 6s]\ O^{2-}$). As the $^8S \rightarrow {}^6S$ spin-flip excitation in the $4f$ shell has been measured to cost about 4 eV [9], a Gd ^8S core is most likely. The coupling of the $4f$ shell to the valence electrons is usually of high spin character. The low-lying excited states are assigned to $4f^7\ 6p \leftarrow 4f^7 6s$ transitions.

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II. EXPERIMENTAL SETUP

The gadolinium oxide anions have been generated in a pulsed-laser vaporization plasma source using helium as carrier gas. After an adiabatic expansion, the anions are accelerated and focused by a Wiley-McLaren ion optic. The anions are mass selected by their time of flight prior to the detachment process. Electrons are detached by a Q-switched Nd:YAG laser pulse (3.495 eV). The kinetic energy of the emitted electrons is analyzed in a magnetic-bottle time-of-flight analyzer [10]. The spectrometer has been calibrated using the atomic lines of Pt. In a conservative estimation, the experimental error of the absolute binding energy is ± 0.1 eV due to the extrapolation of the energy scale to the lower binding energies of GdO (the Pt ground state is at 2.12-eV binding energy). The errors of the relative peak positions are less than ± 5 meV. The vibrational temperatures of the ions in the cluster beam are low due to the cooling process inherent in the adiabatic expansion. Thus, most of the ions are in their vibrational (and electronic) ground state prior to the detachment process.

III. RESULTS

Figure 1 shows the photoelectron spectrum of GdO^- using 3.495 eV photons. The results are summarized in Table I. The adiabatic electron affinity is determined to be 1.19 ± 0.1 eV as revealed by the position of the intense peak near the emission threshold. This peak is assigned to the electronic and vibrational ground state $X\,^9\Sigma^-$ of neutral GdO, which is the final state of the photoemission process. The ground state shows a vibrational progression with the vibrational frequency $\omega_e = 790 \pm 40$ cm^{-1}. This value is in good agreement with previous experimental (813 cm^{-1} in an Ar matrix [8]) and theoretical (786 cm^{-1}, BDF/B88 [3]) investigations.

The lowest electronically excited state is found at 1.42 ± 0.1 eV binding energy. This is assigned to the transition from the anionic ground state into the $a\,^7\Sigma^-$ neutral excited state. The excitation energy has been measured to be 0.23 ± 0.05 eV (1855 ± 40 cm^{-1}). It corresponds to a $6s$ spin-flip transition and can be used to measure the coupling strength of the $4f$ core to the $6s$ valence electron. The mea-

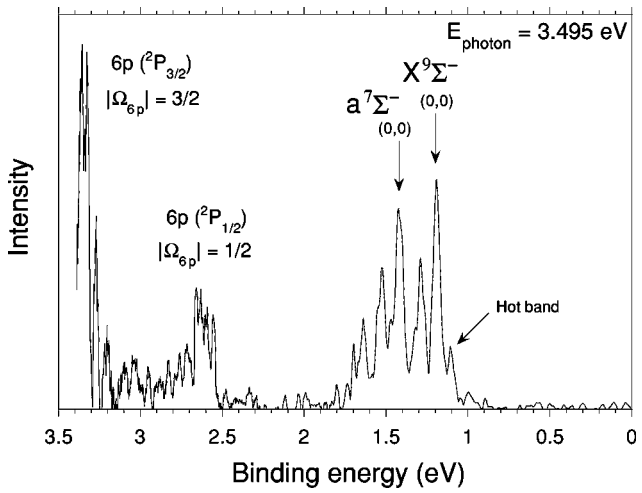

FIG. 1. Photoelectron spectrum of GdO^- taken at 3.495-eV photon energy. The ground-state transition at 1.19 ± 0.1 eV binding energy determines the electron affinity of the molecule. For the ground and the first excited state, vibrational fine structure is resolved.

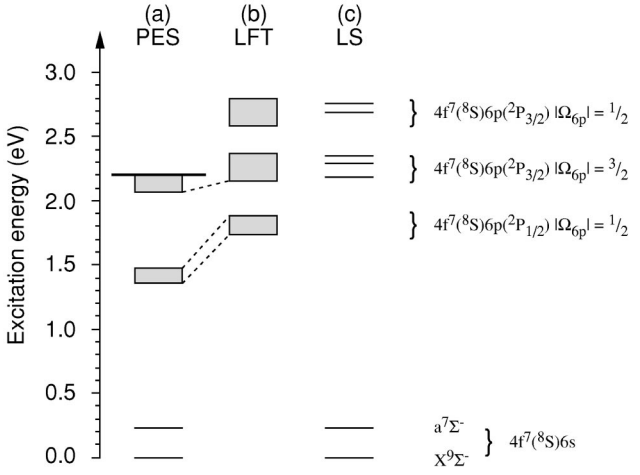

FIG. 2. Comparison of the low-lying electronic states of GdO as revealed by (a) photoelectron spectroscopy (PES), (b) ligand field theory (LFT), and (c) fluorescence excitation spectroscopy [6].

sured value is again in good agreement with previous experimental findings (1837.6 cm^{-1} [6]). From the vibrational progression, a frequency of 887 ± 40 cm^{-1} can be deduced.

The weak emission signal at binding energies below the electron affinity is assigned to a hot band, e.g., the transition from a vibrationally excited anion into the neutral ground state. From this peak, the vibrational frequency of the GdO^- anion is deduced as 702 ± 40 cm^{-1}.

At binding energies between 2.5 and 2.7 eV, a group of states is found in the photoelectron spectrum, and additional peaks appear at binding energies above 3.3 eV. The latter peaks are due to very slow photoelectrons since almost all of the photon energy is left to the GdO molecule as excitation energy. We do not observe the upper edge of this group of states because of the limited photon energy. Both groups of states are interpreted to arise from the $4f^7(^8S)\ 6p \leftarrow 4f^7(^8S)\ 6s$ excitations.

The group of states at 2.6-eV binding energy in the photoelectron spectrum (1.4-eV excitation energy) is interpreted to correspond to the transition into the $4f^7(^8S)\ 6p(^2P_{1/2})\ |\Omega_{6p}|=1/2$ final state, which was not observed in the fluorescence excitation spectrum due to selection rules [6]. Thus, the $6p(^2P_{1/2})\ |\Omega_{6p}|=1/2$ to $6p(^2P_{3/2})\ |\Omega_{6p}|=3/2$ separation is determined to be about 0.7 eV.

Figure 2 shows a comparison of the binding energies found in the present photoelectron spectra (a) with those calculated in a previously developed ligand field approach (LFT) [6] (b) and wavelength-resolved fluorescence spectroscopy (c) [6]. The energy scale for the photoelectron data has been shifted by the measured adiabatic electron affinity (1.19 eV). Thus, in this plot the ground state is located at zero energy, and all energy values correspond to excitation energies. The transitions around 2.3 and 2.7 eV observed in fluorescence excitation have been assigned to the $4f^7(^8S)\ 6p(^2P_{3/2})\ |\Omega_{6p}|=3/2$ and $4f^7(^8S)\ 6p(^2P_{3/2})|\Omega_{6p}|=1/2$ configurations, respectively. Thus, the group of states starting at 3.3-eV binding energy in the photoelectron spectrum (2.1-eV excitation energy) is assigned to the $4f^7(^8S)\ 6p(^2P_{3/2})\ |\Omega_{6p}|=3/2$ final state. Due

TABLE I. Comparison of the results of the present photoelectron spectrum (PES), fluorescence spectroscopy (FS) [6], infrared spectroscopy (IR) [8], and density-functional theory (DFT) [3].

State	Binding energy (eV)	Term energy (eV)		Vibrational energy (cm^{-1})			Δr_e (Å)
	PES	PES	FS	PES	IR	DFT[a]	
$X\,^9\Sigma^-$	1.19 ± 0.1	0.0	0.0	790 ± 40	813	786	0.010
$a\,^7\Sigma^-$	1.42 ± 0.1	0.23 ± 0.05	0.228	887 ± 40			0.009
$6p(^2P_{1/2})\ \|\Omega_{6p}\|=1/2$	2.6 ± 0.1	1.4 ± 0.05					
$6p(^2P_{3/2})\ \|\Omega_{6p}\|=3/2$	3.3 ± 0.1	2.1 ± 0.05	2.182				
			2.290				
			2.353				
$6p(^2P_{3/2})\ \|\Omega_{6p}\|=1/2$			2.685				
			2.760				

[a]BDF/B88.

to the limited photon energy of 3.495 eV, we do not observe transitions into the $4f^7(^8S)\ 6p(^2P_{3/2})\ |\Omega_{6p}|=1/2$ final states. The bold line in Fig. 2(a) labels the top of the photoelectron spectrum.

A Franck-Condon analysis of the vibrational progressions reveals the difference in the equilibrium bond lengths Δr_e of the anion and the respective neutral final state. We find $\Delta r_e = 0.010$ Å for the $X\,^9\Sigma^-$ ground state and $\Delta r_e = 0.009$ Å for the $a\,^7\Sigma^-$ excited state. As expected from the fact that the $X\,^9\Sigma^-$ and the $a\,^7\Sigma^-$ states have the same electronic configuration (distinguished only by the $6s$ spin), r_e is almost the same for the two states. In the simplest case, the additional electron in the anion occupies the $6s$ orbital. Thus, as Δr_e is rather small, a nonbonding character of this orbital can be deduced.

IV. CONCLUSIONS

The photoelectron spectrum of the GdO^- molecule has been measured using 3.495-eV photons. The electron affinity has been measured to be 1.19 ± 0.1 eV. Vibrational fine structure has been resolved for the neutral $X\,^9\Sigma^-$ ($\omega_e = 790 \pm 40$ cm^{-1}) and $a\,^7\Sigma^-$ ($\omega_e = 887 \pm 40$ cm^{-1}) electronic states as well as for the anionic ground state ($\omega_e = 702 \pm 40$ cm^{-1}). Moreover, the excitation energy of the $4f^7(^8S)\ 6p(^2P_{1/2})\ |\Omega_{6p}|=1/2$ states has been measured to be about 1.4 eV.

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